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POLYMORPHISM AND MOLECULAR DYNAMICS IN BERYLLIUM

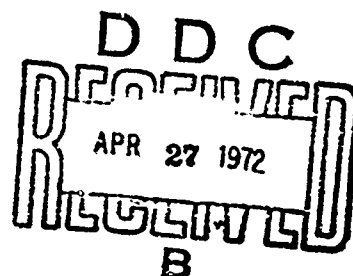
OXYACETATE $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$

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Polymorphism and Molecular Dynamics in Beryllium

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Abstract

The unusual polymorphism of beryllium oxyacetate, $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ was investigated by means of pulsed NMR between -196°C and the melting point (286.7°C). In the α modification of this substance fast methyl group re-orientation takes place, and the spin-spin and spin-lattice relaxation times proved to be insensitive to the presence of the reported second or higher order phase transitions. The onset of a relatively slow motion with an activation energy of 15.5 ± 0.8 kcal/mole was found above the first order phase transition at -148°C , and this motion is likely to be overall molecular tumbling motion. The transition from a high symmetry cubic phase to a lower symmetry orthorhombic structure on raising the temperature is discussed. No self-diffusion is present up to the melting point. The high temperature γ phase of beryllium oxyacetate does not seem to be a plastic crystal as was proposed previously. In light of our results the isotropic optical property by itself is of questionable usefulness as a criterion for plasticity of molecular crystals. Unusual behavior of the spin-lattice relaxation between -20°C and -196°C was determined and the possibility that additional phase transition are present has to be further studied.

INTRODUCTION

The polymorphism of beryllium oxyacetate, $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$, is quite complex and unusual as can be seen from the previous investigations of this compound. From dilatometric,¹ heat capacity^{1,2} and DTA¹ data, second order or higher order phase transitions are known to exist at 42, 77 and 124.5°C, and a first order transition with an entropy change of 15.6 e.u. near 148°C. From ^9Be NQR quadrupole coupling constant measurements,³ additional phase transitions were inferred from discontinuous behavior in the coupling constant vs. temperature plot at 10°C, and between -10°C and -3°C. The different modifications between 10°C and 148°C are known collectively as the α form. All the α forms are most likely cubic although only for the two modifications occurring between 10°C and 77°C is the detailed cubic structure known.⁴⁻⁶ On heating the α form through the phase transition near 148°C, the metastable γ form is obtained and Semenenko⁷ has suggested that it is orthorhombic. The γ phase, once it is obtained, may be supercooled to 110°C before it changes back to the α form. On heating the γ modification of beryllium oxyacetate above 220-230°C and then cooling it to 25°C a relatively stable monoclinic β phase was obtained.⁷ Below +10°C the phase structure of beryllium oxyacetate is as yet unknown.

In past years $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ has been suggested to be plastic crystalline in nature between 160°C and the melting point,⁸ and also has been described as a "pseudo melt."⁷

Revokatov⁹⁻¹¹ has made proton broadline NMR measurements on both single crystal and polycrystalline beryllium oxyacetate samples at selected temperatures. Between 20°C and -200°C the second moment is consistent with

the existence of a reorientation of all methyl groups about their three-fold axes. Above the first order phase transition near 148°C. the single crystal broadline spectrum became independent of crystal orientation.¹¹

Despite the complicated nature of this molecule, the presence of so many crystal structure modifications in beryllium oxyacetate, as well as a transition from a high symmetry cubic structure to a lower symmetry orthorhombic phase on heating this compound gives rise to a special and general interest in molecular and sub-molecular dynamics in beryllium oxyacetate. The proposed plastic crystalline character of the high temperature phase of this substance does not seem to be obvious in light of the conventional plastic crystal definition and has to be reconsidered and reexamined more carefully. Therefore we have carried out temperature dependent measurements of static and rotating frame proton spin-lattice relaxation time (T_1 and $T_{1\rho}$ respectively) and qualitative examinations of the spin-spin relaxation time (T_2) in beryllium oxyacetate. Studies were concentrated especially in the region of known phase transitions between about -20°C and the melting point. Some data were also obtained between -20°C and -196°C.

EXPERIMENTAL

Beryllium oxyacetate was prepared according to literature methods¹² using reagent grade beryllium oxide and acetic acid. The crude product was purified by vacuum sublimation and recrystallized from chloroform before sealing under vacuum in a pyrex sample tube. Microanalysis of our samples showed that they were pure.

The experimental techniques and equipment used in obtaining the proton T_1 and $T_{1\rho}$ vs. T^{-1} data between -196°C and 266.7°C at a frequency of

25.3 MHz have been described previously.¹³ T_2 was estimated qualitatively from the free induction decay duration following a 90° pulse. The rf field amplitude, H_1 , used in our $T_{1\rho}$ experiment was 3 gauss.

RESULTS AND DISCUSSION

α Modifications

The static and rotating frame spin-lattice relaxation time measurements between -20°C and 286.7°C are shown in Fig. 1 as semilog plots versus inverse temperature. T_1 is essentially invariant at about 20 sec between -20°C and 148°C , and no anomalous behavior was found near the second order or higher order transitions at 42°C , 77°C and 124.5°C . $T_{1\rho}$ was not measured in this temperature region for the α modifications since it was relatively long ($>>1$ sec). This relaxation data together with the observed proton powder second moment of 6.90 ± 0.10 gauss²^{9,10} in the temperature range 20 – 135°C , led to a model where only sixfold methyl group reorientations take place with a frequency such that, τ_c , the correlation time for this motion is much shorter than the inverse frequency, ω_0^{-1} , in the entire temperature region in question. Thus the aforementioned phase transitions do not seem to be associated with a change in the type of molecular motion. This is consistent with the x-ray^{4,5} studies where the λ type transition¹ between 32 – 42°C was assigned to a small change in the coordinates of the carboxyl oxygen atoms. In the latter transition temperature range unusual oscillations of the second moments were observed⁹ when the substance had not attained thermal equilibrium. However, when the sample was in a state of thermal equilibrium, the second moment was found to be temperature invariant.⁹

It is unusual to find so many phase transitions in a compound with symmetrical molecules such as beryllium oxyacetate and yet find that motions are not affected. Most likely the complex phase structure is due, to a good extent, to intermolecular methyl group interactions.

Y Phase

Above the first order phase transition near 148°C , T_1 decreases by about a factor of two over a ~ 15 degree temperature interval, although above this region T_1 again becomes temperature independent. The rotating frame relaxation time decreases steeply on raising the temperature from 148°C to the melting point (see Fig. 1). The temperature at which the phase transition occurs in our particular sample is not clear, since previous DTA measurements¹ have shown that this transition may take place at temperatures as low as 133°C and as high as 160°C depending on the treatment of the sample. A single $T_{1\rho}$ measurement was also made in the supercooled Y phase and lies on the same line as observed above the phase transition temperature (see Fig. 1).

Single crystal and powder proton second moment data are available only up to a temperature of about 200°C .⁹⁻¹¹ According to these studies, the powder second moment decreases slightly to 6.2 gauss^2 ⁹ (or $6.3 \pm 0.1 \text{ gauss}^2$ ¹⁰) at the 148°C phase transition and remains at this value at least up to 200°C . Our observations of the free induction decay, or the spin-spin relaxation time (T_2), above 200°C indicated that the proton resonance line does not change up to $\sim 250^{\circ}\text{C}$ where the line narrows gradually up to the melting point (by $\sim 20\%$). Even at the highest temperature of observation the free induction decay could not be approximated by Lorentzian or Gaussian lines. This indicates that the resonance line above 200°C still has some fine structure, most likely due to the close interaction of the three proton sets in the methyl groups, and which was evident also from the broadline studies.⁹⁻¹¹ The possibility that self-diffusion occurs in the Y phase of $\text{Be}_4\text{C}(\text{CH}_3\text{COO})_6$ is ruled out by this moderate line narrowing. The motion responsible for this line narrowing will also be

the effective relaxation process causing the decrease in $T_{1\rho}$ on increasing the temperature in the γ phase.

For reorientations due to dipolar interactions the extended B.P.P. theory^{14,15} in the weak collision limit leads to $T_{1\rho}$ expression as follows:

$$T_{1\rho}^{-1} = C' \left[\frac{5}{2} \frac{\tau_c}{1 + \omega_0^2 \tau_c^2} + \frac{\tau_c}{1 + 4\omega_0^2 \tau_c^2} + \frac{3}{2} \frac{\tau_c}{1 + 4\omega_1^2 \tau_c^2} \right], \quad (1)$$

where ω_0 is the resonance frequency, $\omega_1 = \gamma H_1$, C' is the constant determined by the exact motion present and the other symbols have been defined earlier. The sense of the $T_{1\rho}$ semilog plot indicates that this motion is quite slow, namely $\tau_c \gg \omega_1^{-1}, \omega_0^{-1}$ so equation (1) yields:

$$1/T_{1\rho} = C/\tau_c \quad (2)$$

where $C = C'(11/4\omega_0^2 + 3/8\omega_1^2)$. If we assume the molecular motion to be an activated process so that

$$\tau_c = \tau_0 \exp(E_a/RT), \quad (3)$$

the activation energy, E_a , may be derived directly from the slope of the straight line portion of the $\log T_{1\rho}$ vs. inverse temperature plot employing equations (2) and (3). The activation energy obtained in this manner is 15.5 ± 0.8 kcal/mole. A likely motion for a symmetrical molecule such as beryllium oxyacetate will be an overall molecular tumbling, possibly between a number of allowed orientations. Activation energies for molecular tumbling are known for other large globular molecules such as hexamethylene tetramine¹⁶ (18 kcal/mole) and pentaerythritol¹⁷ (25 kcal/mole). so if we consider the large size of the beryllium oxyacetate molecule, the proposed tumbling activation energy derived in this study is not unreasonable.

The observation that the single crystal line shape becomes orientation independent¹¹ above 148°C indicates that positional randomization has set near the first order phase transition temperature, although the reorientations do not attain a rate sufficient to narrow the resonance line, that is, $\tau_c \gg 1/\delta\omega$, where $\delta\omega$ is the line width in frequency units, until ~250°C is reached. However, the relatively high entropy change of this transition, 15.6 e.u., is difficult to interpret in terms of current theories involving disorder in molecular crystals.^{18,19} If internal disorder (e.g., orientational disorder of the acetate groups) appeared at the phase transition as well as orientational disorder of the entire molecule, such a large entropy change might conceivably be explained. So consideration should also be given to the possibility that the reorientation in the γ phase can be a sub-molecular motion other than tumbling, such as acetate group motion or, a combination of tumbling and the latter motion as well.

Some difficulties arise from the fact that on heating beryllium oxyacetate above 148°C onset of molecular tumbling and orientational randomization occur on one hand, and that the crystal structure is going from the cubic α structure to the lower symmetry orthorhombic γ phase on the other hand. In the absence of motions other than methyl group rotation cubic symmetry can be obtained by various static orientations of the molecules for the α modifications. Indeed the presence of molecular tumbling may lead to positional disorder in the γ phase, but how is it able to reduce the crystal structure symmetry? This may be accounted for by the beryllium oxyacetate molecular shape. The symmetrical molecular core of $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ is composed as follows. A central oxygen atom is surrounded tetrahedrally by four beryllium atoms, each of which in turn is at the center of a tetrahedron consisting of four oxygen atoms. In addition to

Low Temperature (-20°C to -196°C)

Between room temperature and -196°C the proton free induction decay, and, therefore the spin-spin relaxation time, was essentially temperature invariant. Accordingly, the methyl group reorientation takes place at a rate fast enough to narrow the resonance line also in this low temperature region. Revokatov¹⁰ has reported a polycrystalline second moment of $12.0 \pm 0.2 \text{ gauss}^2$ at -196°C in comparison with $6.9 \pm 0.1 \text{ gauss}^2$ at 20°C , a value which is difficult to interpret in light of our observations. The low temperature, -20°C to -196°C , spin-lattice relaxation time versus inverse temperature plot is shown in Fig. 2 as well as the T_1 data in the adjoining temperature region up to 50°C . Generally speaking these spin-lattice relaxation times are relatively long, varying from 6.64 to 44.4 sec. Although one can interpret the spin-lattice relaxation data between -20°C and -156°C in Fig. 2 in terms of a dispersion type curve with a minimum of about 15 sec near -110°C , it does not seem likely to find a motion which corresponds to such a high value for a T_1 minimum. This point cannot be checked from the line width or the second moment, since a negligible change in the latter parameters is expected for a process with such a high T_1 minimum value.

The T_1 behavior in the latter temperature region is quite irregular and does not seem to have any continuous trend. We cannot conclusively explain this irregular temperature dependence of T_1 . However, since so many phase transitions exist at higher temperatures, it is possible that the irregularities in the $\log T_1$ vs. inverse temperature plot are to be associated with phase transitions as well. In particular a phase transition may occur in the interval between -127°C and -140°C , where T_1 increases with decreasing temperature. T_1 reaches its longest observed

this, six peripheral methyl groups stick out from the near-spherical molecular core. It may be that due to these six prominent peripheral methyl groups, relatively slow tumbling of the $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ molecule does not yield spherical symmetry and the molecules do not behave as hard spheres, and a lower symmetry than cubic is accomplished in the γ phase. In view of this it is likely that the orientational randomization indicated by Revokotov¹¹ is still not complete above the first order phase transition.

Although the beryllium oxyacetate molecule could be classified as globular, the substance does not have all the properties usually associated with plastic crystals. Criteria which are used to classify substances as belonging to the class of plastic crystals¹⁰ include, besides a characteristic appearance, a low entropy of fusion of about 5 e.u. or less, a highly symmetrical structure (usually cubic) stable immediately below the melting point, and, the presence of self-diffusion²¹ in the solid state. However, available physical data indicate that for beryllium oxyacetate, the phase below the melting point is orthorhombic, and that the entropy of fusion is 11.5 e.u. The absence of self-diffusion in the high temperature phase of beryllium oxyacetate was revealed in this study and was mentioned previously. These observations constitute conclusive evidence that beryllium oxyacetate is not a plastic crystalline substance under the currently accepted definition. It may be that the characteristic waxy appearance as was noted for beryllium oxyacetate (as well as proper plastic crystals) is due primarily to the presence of orientational randomization. In this light the isotropic optical property by itself is of questionable usefulness as a criterion for plasticity of molecular crystals.

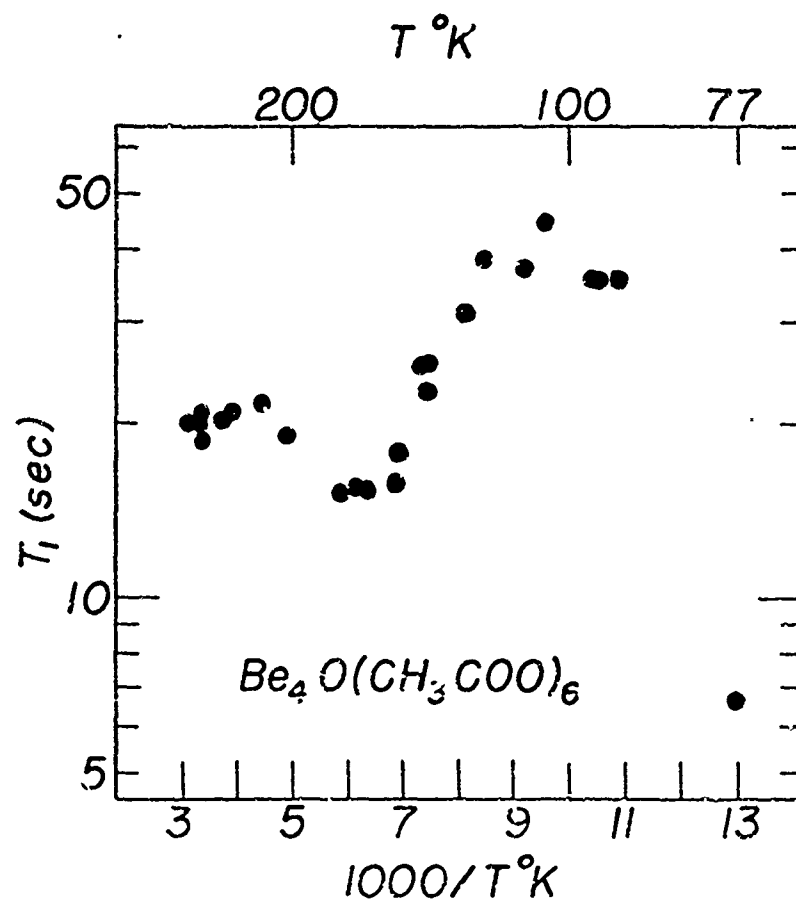


Fig. 2. Temperature dependence of the proton spin-lattice relaxation times (T_1) observed at 25.3 MHz for beryllium oxyacetate between -196°C and 50°C .

value of 44.4 sec at -169°C . Below this temperature T_1 decreases on cooling $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$ down to -196°C . If the onset of molecular motion is associated with the observed decrease in T_1 , values an activation energy of 1-1.5 kcal/mole is estimated from our T_1 data. This value of activation energy near liquid nitrogen temperature is very probable for methyl group rotation about its symmetry axis. If so, a corresponding change in the line width due to this motion is therefore expected well below liquid nitrogen temperatures. A discontinuity in the T_1 curve between -181°C and -196°C would also not be inconsistent with our results.

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FIGURE CAPTIONS

Figure 1: Temperature dependence of the static and rotating frame proton spin-lattice relaxation times (T_1 and $T_{1\rho}$ respectively) observed at 25.3 MHz for beryllium oxoacetate between -20°C and the melting point.

Figure 2: Temperature dependence of the proton spin-lattice relaxation times (T_1) observed at 25.3 MHz for beryllium oxoacetate between -196°C and 50°C .

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The unusual polymorphism of beryllium oxyacetate, $\text{Be}_4\text{O}(\text{CH}_3\text{COO})_6$, was investigated by means of pulsed NMR between -196°C and the melting point (285.7°C). In the modification of this substance fast methyl group reorientation takes place, and the spin-spin and spin-lattice relaxation times proved to be insensitive to the presence of the reported second or higher order phase transitions. The onset of a relatively slow motion with an activation energy of 15.5 ± 0.8 kcal/mole was found above the first order phase transition at -148°C , and this motion is likely to be overall molecular tumbling motion. The transition from a high symmetry cubic phase to a lower symmetry orthorhombic structure on raising the temperature is discussed. No self-diffusion is present up to the melting point. The high temperature γ phase of beryllium oxyacetate does not seem to be a plastic crystal as was proposed previously. In light of our results the isotropic optical property by itself is of questionable usefulness as a criterion for plasticity of molecular crystals. Unusual behavior of the spin-lattice relaxation between -20°C and -196°C was determined and the possibility that additional phase transition are present has to be further studied.